

HYDROGEN PRODUCTION FROM BLACK LIQUOR WASTES

by

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INTRODUCTION

In a typical pulping process, approximately one-half of the raw material is converted to pulp and the other half is dissolved in the spent liquor. In the United States, nearly all of the spent liquor is concentrated and burned to provide part of the energy for the plant. One potential method of utilizing these liquors is to produce gaseous products for fuels, chemicals, and other applications. This suggestion is based on the following reasons: (1) the carbonaceous material of black liquor is well dispersed, (2) the black liquor contains considerable amount of alkali metals, which are known to have excellent catalytic effect on gasification, and (3) the concentrated black liquor contains about 40 to 60 percent of water, which can be converted to steam for the carbon-steam gasification reaction.

Because of the presence of carbonaceous material and water in the black liquor, it is suspected that the following water-carbon reactions would predominate:



Normally, the hydrogen concentration in the product gas should not exceed a certain limit imposed by thermodynamic equilibrium. For example, for a typical sodium-base spent liquor, the hydrogen concentration in the pyrolytic gasification products at 1000 K and ambient pressure will not exceed 60 percent in volume (1). However, in the presence of a CO_2 -removal reagent, such as NaOH or CaO, etc., the equilibrium can be shifted

to drive reaction (2) toward completion. This would maximize the hydrogen yield, and, at the same time, reduce CO and CO₂ concentrations in the product gas.

The feasibility of utilizing the spent liquor via pyrolytic gasification at nearly atmospheric pressures has been demonstrated by Prahacs et al^{(1), (2)}. They concluded that the Na-base liquor gave highest yields of hydrogen and carbon monoxide. However, the hydrogen in the product gas was generally in the range of 50-60 percent by volume. The objective of this paper is to demonstrate experimentally the technical feasibility of producing hydrogen-rich gas by pyrolytic gasification of black liquor. Sodium hydroxide was selected as a CO₂-removal reagent for convenience of handling in a microreactor used in this study.

EXPERIMENTAL

The gasification experiments were conducted in a batch reactor system as shown in Figure 1. The reactor was made of a 12-inch-long 3/4-inch Inconel pipe (I.D. 0.742", O.D. 1.050"). Helium was used as an inert tracer to provide a material balance from which gasification yield was estimated.

In a typical experiment, the reactor was brought to the selected reaction temperature, evacuated, and then pressurized to 20 psig with helium. With valves V6 and V7 closed, a measured amount of water (0.5 cc, typically) was loaded into the sample reservoir through V5 by means of a hypodermic syringe and V5 was closed. The free space above the water sample in the reservoir was pressurized to 300 psig with argon (to serve as piston gas) and isolated by closing V4 before the water was forced into the heated reactor by opening valve V6 and immediately closing it. This provided a steam environment for gasification. With the same procedure, a measured amount of black liquor (2.0 cc) was then injected into the steam-filled reactor, except that 600 psig of helium pressure was

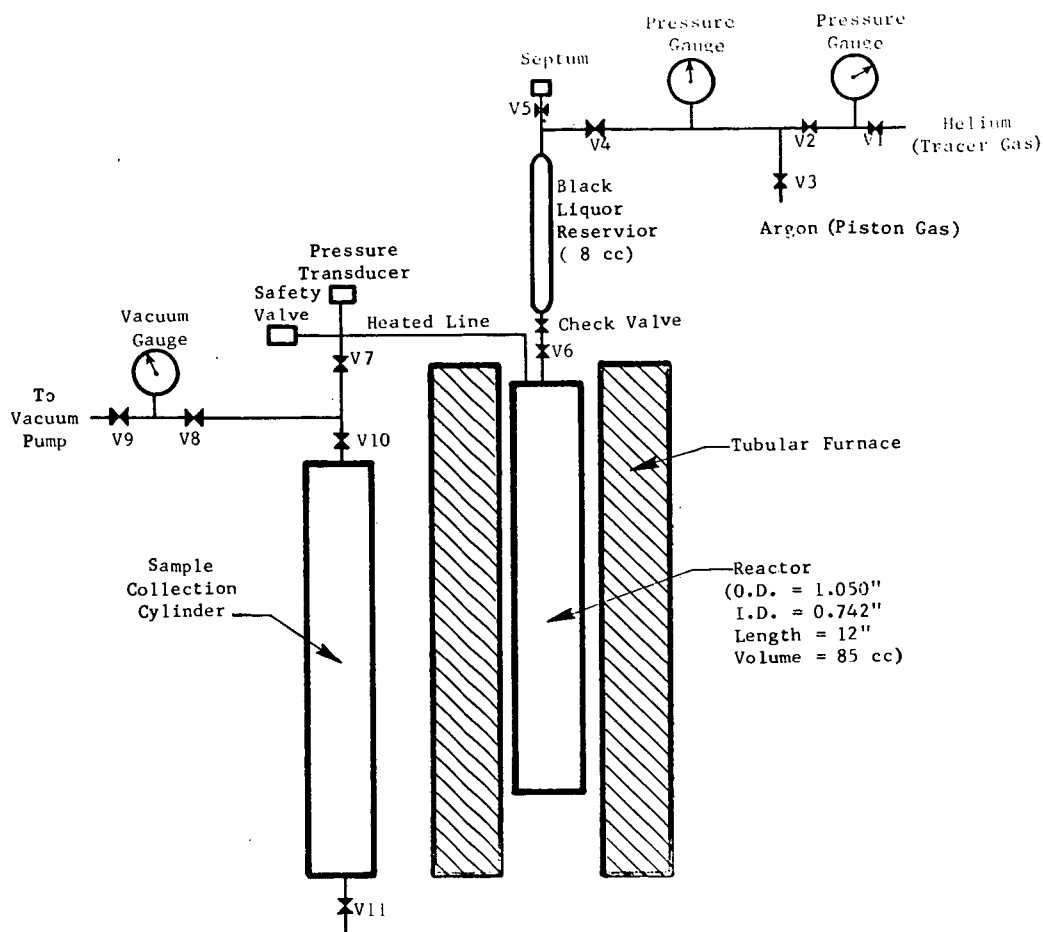


FIGURE 1. EXPERIMENTAL SETUP FOR BLACK LIQUOR GASIFICATION

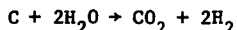
used as a piston gas. Vaporization of the solution took place almost instantaneously. After the predetermined reaction period, the products were collected by opening valves V7 and V10 to transfer the sample to the collection cylinder. The collected gaseous reaction products were analyzed by gas chromatography and mass spectroscopy.

All experimental tests to be discussed in this paper were conducted at 800 C. Two minutes were selected as the reaction time.

The sodium-base black liquor used in this study contained 15.6 percent by weight organic carbon. To investigate the addition of CO₂-removal reagent, various amounts of sodium hydroxide were added to the liquor at Na/C mole ratios of 0.00, 0.38, 0.77, and 1.15, where Na is moles of added sodium and C is moles of organic carbon in the liquor.

RESULTS

The results from the above-mentioned experiments are shown in Table 1 and Figures 2 and 3. The degree of gasification was estimated by assuming that hydrogen and carbon dioxide is produced according to the carbon steam reaction:



Therefore, for every two moles of hydrogen produced, one mole of organic carbon in the black liquor should be gasified. The carbon dioxide thus formed would react with NaOH to form sodium carbonate, up to the limit imposed by the quantity of NaOH added and/or already present in the black liquor. The following observations were made: the main reaction products were found to be hydrogen, methane, carbon dioxide, and carbon monoxide; very small amounts of C₂-C₆ hydrocarbon (rarely exceeding 1.3 percent total) were observed; the concentration of hydrogen in the gaseous products was very high in all experiments, ranging from 62 to 88 volume percent.

TABLE 1. RESULTS OF PYROLYTIC GASIFICATION
OF BLACK LIQUOR

| Run No. | PG-01 | PG-02 | PG-03 | PG-04 |
|--|--------|--------|--------|--------|
| Temp (C) | 800 | 800 | 800 | 800 |
| Na/C Mole Ratio in Feed ⁽¹⁾ | 0.00 | 0.38 | 0.77 | 1.15 |
| Product Yield (g-mole/1000 cc of as-received liquor) | | | | |
| H ₂ | 6.85 | 11.96 | 16.77 | 18.35 |
| CO | 0.45 | 0.36 | 0.40 | 0.12 |
| CH ₄ | 1.88 | 2.70 | 2.01 | 1.90 |
| CO ₂ | 1.69 | 1.30 | 1.00 | 0.42 |
| C ₂ H ₄ | 0.008 | 0.012 | 0.007 | NIL |
| C ₂ H ₆ | 0.039 | 0.087 | 0.012 | 0.051 |
| C ₃ H ₆ | 0.002 | 0.007 | 0.003 | 0.006 |
| C ₃ H ₈ | NIL | 0.005 | NIL | NIL |
| C ₆ H ₆ | 0.005 | 0.12 | 0.077 | 0.08 |
| Product Composition (%) | | | | |
| H ₂ | 62.4 | 72.3 | 82.7 | 87.7 |
| CO | 4.1 | 2.2 | 2.0 | 0.57 |
| CH ₄ | 17.1 | 16.3 | 9.9 | 9.1 |
| CO ₂ | 15.4 | 7.9 | 5.0 | 2.0 |
| C ₂ H ₄ | 0.07 | 0.07 | 0.03 | NIL |
| C ₂ H ₆ | 0.35 | 0.53 | 0.08 | 0.24 |
| C ₃ H ₆ | 0.01 | 0.04 | 0.02 | 0.03 |
| C ₃ H ₈ | NIL | 0.03 | NIL | NIL |
| C ₆ H ₆ | 0.6 | 0.72 | 0.38 | 0.38 |
| | 100.33 | 100.09 | 100.11 | 100.02 |
| Percent Gasification (based on carbon input) | 40.0 | 64.0 | 72.5 | 75.6 |

(1) Na-content refers to the amount of NaOH added to the liquor.
C-content is 15.6 wt %.

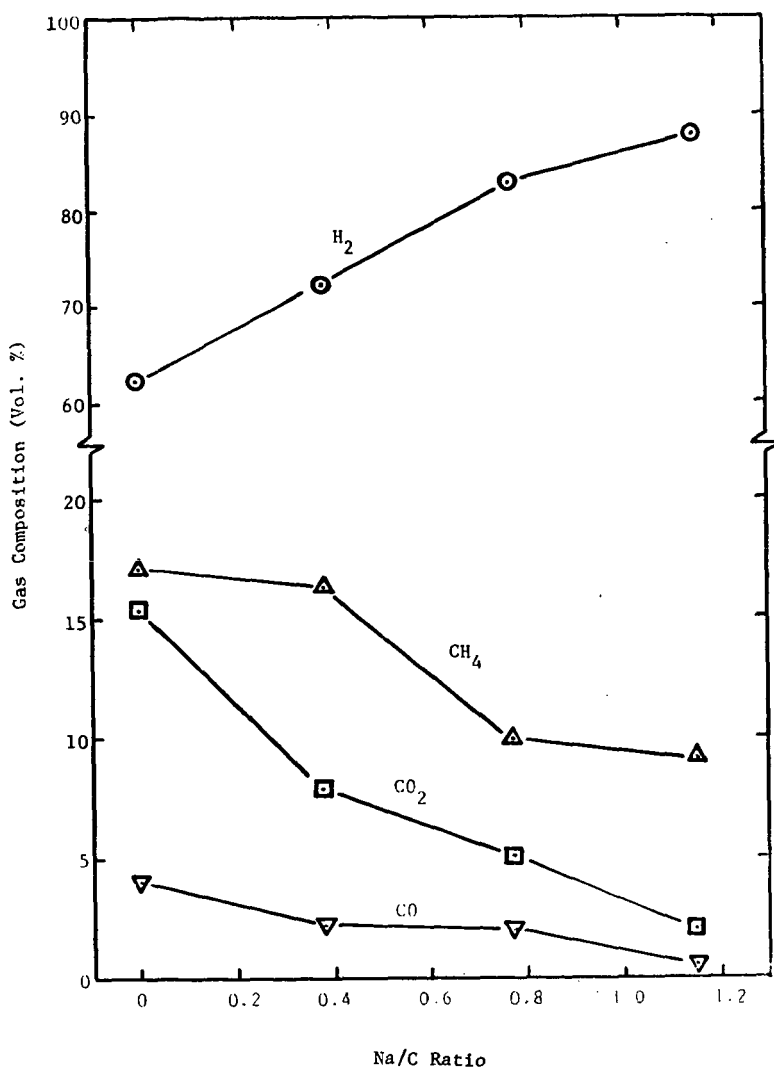


FIGURE 2. PRODUCT GAS COMPOSITION

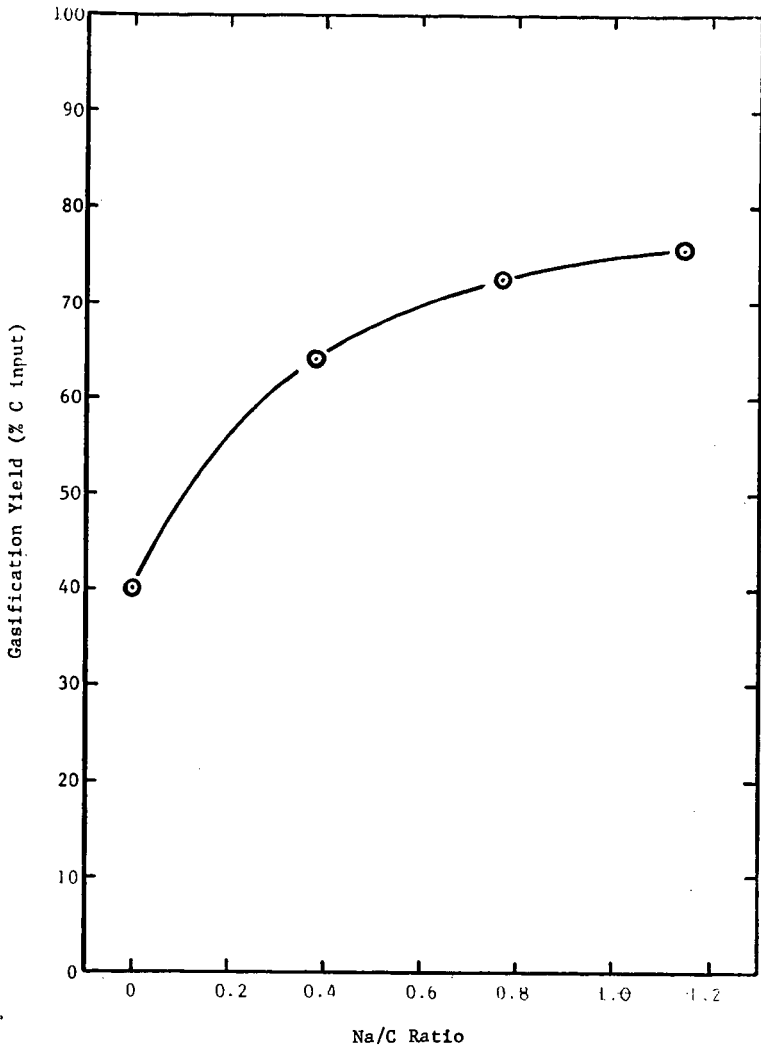


FIGURE 3. GASIFICATION YIELD

There are two striking effects of the added caustic soda on the gasification of black liquor. The first is the product-gas distribution, and the second is the total gasification yield. As shown in Figure 2, the hydrogen content of the gas increased with increasing Na/C ratio; about 88 percent of hydrogen was obtained with Na/C ratio of 1.15 as compared to 62 percent when no free NaOH (Na/C = 0.00) was added to the black liquor. Also, the CO and CH₄ concentrations, in general, decreased progressively with increasing Na/C ratio. The total gasification yield as a function of Na/C ratio is shown in Figure 3. Significant increases in total gasification yield with increasing Na/C ratio were observed. About 76 percent of conversion can be obtained at Na/C of 1.15, as compared to 40 percent, when no free NaOH was added to the black liquor. This suggests that the added alkali metal greatly enhances the gasification reaction.

CONCLUSIONS AND DISCUSSION

In conclusion, the production of hydrogen in concentrations greater than 85 percent in the gas from pyrolytic gasification of black liquor is technically feasible. The addition of caustic soda to the black liquor not only enhances the gasification reaction, but also increases the hydrogen concentration in the product gas. Other reagents, such as calcined limestone or dolomite, may be substituted for the caustic soda.

Thus, a waste material, which presents a disposal problem and a potential pollution hazard, can be converted to products for useful fuels, chemical feedstocks, and/or applications.

LITERATURE CITED

- (1) Prahacs, S. and Gravel, J.J.O., "Gasification of Organic Content of Sodium-Base Spent Pulping Liquors in an Atomized Suspension Technique Reactor", Ind. & Eng. Chem. Proc. Des. & Devel., 6 (2), P 180 (1967).
- (2) Prahacs, S., "Pyrolytic Gasification of Na-, Ca-, and Mg-Base Spent Pulping Liquors in an AST Reactor", Fuel Gasification, Advances in Chemistry Series, Vol. 69, American Chemical Society Publications (1967).